Bush :-

Potassium cyanide titration of nickel ...

THE POTASSIUM CYANIDE TITRATION OF NICKEL IN NICKEL-CHROMIUM STEELS

BY

ALEXANDER T. BUSH

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMISTRY

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1919

UNIVERSITY OF ILLINOIS

August 17 1919

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Alexander T. Bush

ENTITLED The Potassium Cyanide Titration of Nickel

in Nickel-Chromium Steels

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemistry

S. A. Braley
Instructor in Charge

APPROVED: W. A. Noyes

HEAD OF DEPARTMENT OF Chemistry

TABLE OF CONTENTS.

P U R P O S E

It has been noticed that, in titrating nickel by the potassium cyanide method for the determination of nickel, in nickel-chromium steels it is very hard to determine the end point because the chromium has a darkening effect on the solution, and even in some cases effects the opacity to such an extent that at times it is impossible to see through. It is the purpose of this paper to present a method by which it is possible to clear the solution to be titrated to such an extent that it will be perfectly possible to obtain the end point of "crystal clear" and arrive at the correct amount of nickel within a reasonable length of time to make it practicable for use in steel laboratories where time as well as accuracy is a factor.

HISTORY OF THE DETERMINATION.

The first method that is at all practical for the volumetric determination of nickel in steel was published be E.D. Campbell and W.H. Andrews (*1). This is really a revision of a former method published by E.D. Campbell a few months before, but the first method was so impractical that the author hastened to improve on it.

The principle of this method, as is the principle now, is the fact that as long as nickel is present uncombined with the potassium cyanide the cyanide will not dissolve the indicator of silver halide. As soon as all the nickel is in combination with the potassium cyanide, the cloudiness caused by the silver halide will disappear, and the solution will become "crystal clear". This is the end point.

In the method presented by the above mentioned men, a one gram sample of the steel is dissolved in nitric acid. The nickel is then precipitated from the solution with potassium xanthate, filtered and washed with more of the precipitating solution. Copper is also precipitated with the nickel, and a little iron is occluded. (The presence of copper in the alloy steels of that time was a source of much trouble to the analyst). The precipitate is then dissolved in nitric acid, and the copper removed by precipitation with hydrogen sulfide. This precipitate is filtered off, and the filtrate treated with an oxidizing agent to oxidize the iron. The solution made ammonical and the precipitate of ferric hydroxide is filtered off. The solution now ready for titrating is treated with silver nitrate

and potassium iodide, and titrated to a clear solution with standard potassium cyanide.

The length of this procedure requires much care by the operator to prevent loss. However very good results were obtained. The authors claim two hours as the time necessary to prepare the solution for titration.

In 1889 Thomas Moore published an article (*2) on the cyanide method for the determination of nickel. However he uses as an indicator cupric ferro-cyanide, and the change in the color of this compound gives the end point. In this method the titration is made after the nickel has been isolated, but no provisions are made for isolating it.

In 1895 (*3) the same author published an article in which he admits the weakness of his former method, and substituted silver nitrate and potassium iodide as indicators for the unsatisfactory cupric ferro-cyanide. In the main this is the same method as that of Campbell's (*1), but as in the case with his first procedure he does not give a method for separating the nickel from the other elements, nor does he apply it to steel analysis.

Brearley and Jervis (*4) introduce the use of tartaric acid as a means of preventing the precipitation of the other metals in solution. They also advocate the use of potassium iodide and silver nitrate as indicators. However as a whole their paper is only on the effects of the presence of other elements on the method, and is not a method for the analysis of steel.

They also notice the trouble that chromium gives in this determination. However they attribute this to the effect of the tartaric acid, and give as a means of avoiding such interference

the conversion of the chromium oxide salts to chromic acid salts. This is the basis of the method to be presented.

In conclusion they account for the discrepancies in results by the then existing methods by the fact that nickel is likely to be occluded when the other metals are precipitated and removed.

In 1907 C.M. Johnson (*5) presented a method for nickel which is the same (in all but a few minor points) as that now in general use in steel laboratories. He dissolved one gram of steel in ten cubic centimeters of hydrochloric acid (1:1). When action had ceased he added ten cubic centimeters of nitric acid (Sp.Gr. 1.20) and evaporated the solution to half volume and added sixteen cubic centimeters of dilute sulfuric acid and three grams of citric acid. (Either citric or tartaric may be used to prevent the precipitation of iron) The solution is then ready for titration. Add the silver nitrate and potassium iodide and titrate with standard potassium cyanide solution. The solution to be titrated was often dark in color, and often artificial light had to be used to recognize the end point. The amount of citric acid which was added to the solution was decreased, but this increased the opacity of the solution, so the addition of more than three grams was tried. This gave increasing clearness until a maximum of twelve grams had been added. This was decided as being the correct amount needed, as furthur additions did not lighten the color. This is the amount used in most of the modern methods.

The equations which explain the action of the potassium cyanide are given by this author, and agree with those mentioned by other investigators:

(1) $Ni(NO_3)_2 + 4KCN = Ni(CN)_2.2KCN + K(NO_3)$

(2) $AgNO_3 + 2KCN = AgCN.KCN + K(NO_3)$

Mr. Johnson also encountered difioulties when nickel is determined in the presence of chromium. He claims to have cleared the solution sufficiently by means of citric acid to get good results. For this he used twenty four grams of citric acid when a one gram sample is taken.

His data indicates his work to be very accurate, <u>but</u> he used potassium dichromate as a source of the chromium present in his tests, and states "that in the hands of a trained man this method is very accurate". However it is very possible that when chromium is encountered in the ordinary routine analysis it occurs as a compound with iron, and often the steel will not go into solution unless sulfuric acid is used. Thus his experiments will not exactly fit with experience of the routine chemist.

However he concludes that the trouble encountered in the presence of copper was unnecessary. He states that in the great number of steels he has analyzed, there was only one case in which the copper was over nine-hundredths of one percent, and that was one heat of a very low carbon steel from an open hearth furnace. (At this time most of the alloy steel was made in a crucible).

In 1908 E.D. Campbell and Walter Arthur (*6) revised the method of Campbell (*1) and claim that Campbell ought to be given credit for the cyanide method for nickel. These authors first trace the improvement of the method and advocate the use of sodium pyrophosphate to prevent the precipitation of iron when the solution is made slightly ammoniacal. Their method is as follows:

One gram of steel is dissolved in from ten to fifteen cubic centimeters of nitric acid (SP. GR. 1.20). After complete solution, six to eight cubic centimeters of hydrochloric acid (1:1) are

added, and the same amount of sulfuric acid (1:1) and the solution boiled until the white fumes of sulphur tri-oxide are given off. It is then cooled and thirty or fourty cubic centimeters of water are added and again boiled until all the ferric sulphate is dissolved. If it is not clear it is filtered into a four-hundred cubic centimeter beaker. A freshly prepared solution of thirteen grams of sodium pyrophosphate in about sixty cubic centimeters of water is added and the solution cooled. Ammonia is added until the solution tests alkaline, but does not smell of ammonia. This much ammonia will dissolve most of the precipitate of ferric ~~hydroxide~~ pyrophosphate. The solution is gently heated until the remainder of the precipitate has dissolved and cool to room temperature. The solution is then ready to be titrated, using silver nitrate and potassium iodide as indicators.

This method is claimed to be accurate provided there is no copper or chromium present. The copper can be removed by leaving it undissolved and filtering it off, but this step is shown to be unnecessary since Johnson showed that very little copper was present in alloy steels. The chromium is removed by oxidizing it(while dissolving the sulphates) by adding potassium permanganate until a precipitate of manganese dioxide is produced, and filtering it off with the manganese dioxide. The filtrates are then concentrated to a volume of sixty cubic centimeters and the pyrophosphate is added and the process is carried on as above.

This paper is the last one that has appeared in the journals but Treadwell and Hall (*7) give as the standard method for nickel one similiar to the above, but make a note that" some chemists prefer to use citric or tartaric acid to prevent the precipitation

of the iron by ammonia.

In 1915 the United States Steel Corporation (*8) printed a pamphlet which gives the standard method for all the elements determined in steel, and gives as the standard method for nickel:

One gram of steel is treated with thirty cubic centimeters of nitric acid (Sp. Gr. 1.20). Heat is applied when all action has ceased, and ten cubic centimeters of hydrochloric acid (1:1) is added. The solution is evaporated to a volume of about ten cubic centimeters.Fifty cubic centimeters of a solution of two hundred grams citric(or tartaric) acid, two hundred cubic centimeters sulfuric acid (1:1) and eight hundred cubic centimeters of water, are added and the solution cooled to room temperature. The acid is neutralized with ammonia and three cubic centimeters in excess are added. Again cool to room temperature and titrate in the usual manner using silver nitrate and potassium iodide as indicators. Chromium is, as usual, bothersome, and in this case it is avoided by the use of twice the usual amount of the citric-sulfuric acid solution.

A more recent method (not in published form) in use in some steel laboratories of the Corporation and Navy department is practically the same as the one just given, but is a little more rapid is as follows:

One gram of steel is dissolved in a five hundred cubic centimeter flask with twenty cubic centimeters of nitric acid (Sp.Gr. 1.20). When action has ceased add five cubic centimeters of hydrochloric acid (1:1) and evaporate to half volume. Add twenty-five cubic centimeters of ammonia (1:1) and cool in a water bath. Add two cubic centimeters of standard silver nitrate solution from a burrette. This gives a cloudy precipitate of silver

chloride. Dissolve this by adding ammonia to the solution and then add two cubic centimeters in excess. Add ten cubic centimeters of potassium iodide, which gives a precipitate, similiar in appearence to the silver chloride, of silver iodide. Titrate with standard potassium cyanide until clear. Back titrate with silver nitrate until the cloudy precipitate reappears and again clear with potassium cyanide, this time being careful not to run past the end point of "crystal clear".

This method is not quite as accurate as the other methods frequently used, and unless the analyst is experienced, the end point is rather hard to detect. Never-the-less in this manner one can make a determination, correct within three-hundredths of one percent, in less than ten minutes.

A DISCUSSION OF THE THEORY INVOLVED.

In the case of nickel-chromium steels it has been noticed that the solution to be titrated has a much darker color, and in steels with a very high chromium content a cloudiness is formed that can not be cleared up by the addition of ammonia. This may be attributed to the presence of chromium as a colloidal precipitate. The darker color or cloudiness interferes so much with the detection of the end point that checks can not be made to bear out the original determination. As a result of this, nickel must be determined by one of the longer methods.

When chromium nitrate is heated in the presence of nitric acid and air it will be converted to chromic oxide (Cr_2O_3). This is insoluable in nitric acid and only slightly soluable in hydrochloric acid. Because of this, if the solution of the steel in nitric acid is evaporated to dryness and heated, nearly all of the chromium will be converted to the insoluable oxide and when the oxides of all the elements present are treated with nitric and hydrochloric acids for a short time and the solution filtered, the insoluable chromic oxide will remain on the filter paper. This is the proposed method for removing the chromium.

Since the last mentioned method is considered sufficiently accurate, the chance of error in the method to be proposed lies in the heating and re-dissolving. As stated, some of the heated residue is not dissolved by the nitric and hydrochloric acids, and it is possible that some of the other elements present might also remain undissolved. With this in view, the filter paper containing the

residue was digested with nitric and hydrochloric acids until disintegrated. The pulp filtered off, and the filtrate made ammoniacal. There was no precipitate of ferric hydroxide, showing that no iron remained undissolved. To the solution was added acetic acid and the di-methyl-glyoxime test for nickel carried out. In the majority of cases no test for nickel was obtained. Those showing the presence of nickel gave such slight precipitate that it could not be accurately filtered off and weighed. These tests were repeatedly made, and in no case was any appreciable amount of iron nor nickel present. These tests show that all the iron and nickel are redissolved when the heated residue is taken up in the acids.

The next point in the consideration of the method to be proposed is the time factor. The increase of time necessary to carry out this step will be the time required to evaporate fifteen cubic centimeters of acid to dryness, three minutes of heating, and about ten minutes to evaporate the filtrate to a smaller volume. All this depends on the attentiveness of the analyst, and should not take more than fifteen minutes in all. The manipulation will be taken up in detail in the explanation of the method.

The accuracy of the method to be proposed will be explained with the experimental data.

THE PROPOSED METHOD.

The method proposed is as follows:

Dissolve a one gram sample of steel in fifteen cubic centimeters of nitric acid. (1:20) . The solution is effected in a wide mouthed flask or beaker. (These are called filtering flasks or conical beaker flasks and are of three hundred cubic centimeter capacity) The solution is evaporated to dryness on the hot part of a hot-plate. When the solution begins to spatter the beaker is moved to the cooler part until spattering ceases. The flask is then put back on the hottest part of the plate until all fumes of nitric acid are driven off and set aside to cool until fifteen cubic centimeters of nitric acid (1:20)can be added without danger of cracking the beaker. After the addition of the acid it is put back on the plate and five cubic centimeters of hydrochloric acid (1:1) are added. Heat until all the soluble matter seems to have dissolved. About two minutes of boiling will effect this. Add a little water to dilute the acid enough to prevent its attacking the filter paper and filter into a five hundred cubic centimeter flask. Wash until the paper and beaker are free from acid. Usually three small portions of water are enough for that. Put the flask back on the hot-plate and evaporate to about fifteen cubic centimeters volume. Proceed from this point as given in the last method, adding citric acid and ammonia etc.

The solutions used in this method are the same as those used for any nickel determination by the steel corporation and in most of the other methods. They are as follows:

NITRIC ACID of specific gravity of 1.20.

HYDROCHLORIC ACID (1:1)

One volume of concentrated acid to one volume of water.

CITRIC ACID.

250 grams of pure acid crystals dissolved in a liter of water/

AMMONIA (1:1)

One volume of concentrated ammonia water dissolved in one volume of water.

SILVER NITRATE SOLUTION (Standard)

5.85 grams of chemically pure silver nitrate crystals dissolved in one liter of water.

POTASSIUM IODIDE SOLUTION (Indicator)

2 grams of chemically pure potassium iodide dissolved in one hundred cubic centimeters of water.

POTASSIUM CYANIDE SOLUTION (Standard)

6.775 grams of chemically pure potassium cyanide dissolved with 7.5 grams chemically pure potassium hydroxide in 1500 cubic centimeters of water.

One cubic centimeter of the silver nitrate solution is supposed to equal one cubic centimeter of potassium cyanide solution. The potassium cyanide is supposed to be of such a strength that one cubic centimeter will be equivalent to one tenth of one percent nickel.

Since it is very hard to make up these solutions exactly normal, the ratio of the silver nitrate to the potassium cyanide is found by back titrating, and the steels with a known content of nickel

are determined and a normality factor is calculated for the potassium cyanide from these results. A different factor is obtained with different alloy steels, so a factor for each steel must be determined. (That is for nickel steels, for chromium-nickel steels, etc.)

To calculate the percent of nickel form the data, subtract the potassium cyanide equivalent of the silver nitrate used from the total amount of potassium cyanide used, and multiply by the normality factor.

EXPERIMENTAL DATA

Tests as to the efficiency of the proposed method as made at this university were performed on three samples of nickel-chromium steel of the following composition:

	Sample (1)	Sample (2)	Sample (3)
Carbon	.60%	.375%	.68%
Silicon	.230%	.096%	.435%
Manganese	.88%	.214%	.80%
Sulphur	.016%	.025%	.033%
Phosphorus	.018%	.018%	.036%
Chromium	1.80%	.89%	2.48%
Nickel	2.45%	1.62%	3.20%

Other tests were made with samples met in ordinary routine analysis while working at the United States Naval Ordnance Plant, South Chareston, West Virginia.

The first set of experiments performed to prove the adaptibility of the proposed method were to show its accuracy. Sample (1) was used with out heating to give a factor for the potassium cyanide solution and to obtain a ratio between the silver nitrate and potassium cyanide. The same sample was determined by the heating method to give a factor for that procedure, the factor resulting being the same in both cases. The varience in results using both methods shows the accuracy of the proposed method.

The results are as follows:

Sample (1)

	No Heating	Heating
Test (1)	2.45 % Ni	2.45 % Ni
" (2)	2.48 % "	2.46 % "
" (3)	2.41 % "	2.44 % "
" (4)	2.51 % "	2.43 % "

The correct amount of nickel is 2.45 %.

Sample (2) was given as an unknown, and was determined by the two methods:

Sample (2)

	No Heating	Heating
Test (1)	1.58 % Ni	1.60 % Ni
" (2)	1.58 % "	1.61 % "
" (3)	1.64 % "	1.62 % "
" (4)	1.67 % "	1.62 % "
Average	1.62 % Ni.	1.61 % "

The correct amount of nickel in this steel was 1.62 % but since the chromium was only .89% the heating was really unnecessary.

Sample (3) was tested in the same way:

Sample (3)

	No Heating	Heating
Test (1)	3.10 % Ni	3.21 % Ni
" (2)	3.15 % "	3.23 % "
" (3)	3.23 % "	3.23 % "
" (4)	3.25 % "	3.19 % "

The correct amount of nickel is 3.20 % .

DISCUSSION OF RESULTS.

The figures given in the experimental data were not all the tests made, but are given as typical cases from samples all determined at the same time. They show the improved method to be accurate. They also illustrate very clearly the difficulty experienced in making checks, showing how hard it is to identify the end point unless the chromium is removed or the solution made lighter in color. In high chromium steels (samples (1) and (3) are examples) the solution never becomes clear unless the heating process is used. However with lower chromium content steels as sample (2) the end point can be easily seen without the heating.

As shown above there is no nickel left in the residue from the heating since di-methyl-glyoxime gives no test when used according to the requirements for a nickel test.

A few tests were performed adding insoluable chromic oxide to the nitric acid solution before evaporating to dryness and subsequent heating. Results on the amount of nickel found are as follows:

Test	(1)	2.46 % Ni.
"	(2)	2.46 % "
"	(3)	2.44 % "

These were performed on sample (1) in which there was 2.45 % nickel. This shows the method is accurate no matter how much chromium might be present, for in these tests chromium to the amount of more than one gram was added to a solution of one gram of steel, thus making a solution in which the chromium would be much greater than if the steel contained fifty percent of it.

As with the other results listed, these are examples taken

from a series of tests, which all bear these figures out.

The qualitative test for nickel was applied to the residue in the above case, and a negative test was found in every case, showing that none of the nickel was left undissolved when the residue was taken up in nitric and hydrochloric acids.

(In these tests the solution before evaporating and heating was absolutely opaque, but after heating and filtering the resulting solution was a light yellow in color and clear.

CONCLUSION.

In conclusion it is now possible to state, that the method presented herein is accurate and rapid. The accuracy being proven by the fact that the end point is more pronounced, all the nickel is returned to the solution to be titrated, and that the solution is free from any cloudiness and is of a color light enought to be titrated. The rapidity being shown by the slight deviation from the fast method now in general use.

B I B L I O G R A P H Y.

(*1) E.D. Campbell and W.H. Andrews,
Journal of the American Chemical Society,
Vol. 17, Page 126, 1895.

(*2) Thomas Moore,
Chemical News,
Vol. 59, Page 160, 1889.

(*3) Thomas Moore,
Chemical News,
Vol. 72, Page 92, 1895.

(*4) Brearly and Jervis,
Chemical News,
Vol. 78, Page 177 and 190, 1898.

(*5) C.M. Johnson,
Journal of the American Chemical Society,
Vol. 29, Page 1201, 1907.

(*6) E.D. Campbell and Walter Arthur,
Journal of the American Chemical Society,
Vol. 30, Page 1116, 1908.

(*7) Treadwell and Hall,
Analytical Chemistry, (Quantitative)
Vol. 2, Page 729, 1911.

(*8) Chemists Committee, United States Steel Corporation,
Methods for the Analysis of Alloy Steels, 1915.